

Roles of lattice oxygen in V_2O_5 and activated coke in SO_2 removal over coke-supported V_2O_5 catalysts

Yong Xiao^{a,b}, Qingya Liu^c, Zhenyu Liu^{a,c,*}, Zhanggen Huang^a,
Yanxia Guo^a, Jianli Yang^a

^a State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Taiyuan, Shanxi 030001, PR China

^b Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China

^c State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

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Abstract

This paper systematically investigates the roles of lattice oxygen in V_2O_5 and activated coke over coke-supported V_2O_5 catalysts in SO_2 removal process at 200 °C. The results show that one SO_2 molecule reacts with one O atom in a surface V_2O_5 molecule to form an intermediate (a $VOSO_4$ -like structure), which then reacts with gaseous O_2 to form sulfur species (SO_3 or H_2SO_4 in the presence of H_2O) and V_2O_5 . The SO_3/H_2SO_4 migrates over the coke surface and stores in the pores in the vicinity of V_2O_5 sites. Mineral matters, oxygen and nitrogen species in the activated coke are unfavorable to migration of SO_3/H_2SO_4 . The pores effective for storage of SO_3/H_2SO_4 are those less than 1 nm in size.

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1. Introduction

SO_2 and NO in flue gas are major air pollutants and must be removed before emission. Among various emission control technologies [1–3], activated coke (AC) and activated carbon fiber (ACF) were found to have good SO_2 removal activities at temperatures below 100 °C [3–8]. However, flue gases are usually maintained at temperatures around 150 °C or higher for self-ventilation. This makes the use of AC/ACF-based technologies difficult because flue gases must be cooled down for SO_2 removal and then be heated up for ventilation.

Our recent work [9,10] found that supporting V_2O_5 onto an AC (V_2O_5/AC) results in high activities in SO_2 removal as well as in selective catalytic reduction (SCR) of NO_x by NH_3 at temperatures around 200 °C. This V_2O_5/AC -based technology not only allows flue gas self-ventilation, but also solves NO pollution simultaneously. Studies regarding SCR reaction over

V_2O_5/AC have been reported in our earlier works [11,12]; SO_2 removal over V_2O_5/AC is studied in detail in this paper.

The SO_2 removal process over porous carbon materials was found involving a number of steps: adsorption of SO_2 , oxidation of SO_2 to SO_3 , reaction of SO_3 with H_2O to form H_2SO_4 , and storage of H_2SO_4 in pores [4,13,14]. Surface oxygen groups were found to be important for absorption and oxidation of SO_2 [13,15], and surface area and pore volume were important for absorption of SO_2 and storage of H_2SO_4 [4,16,17]. Since storage of H_2SO_4 or SO_3 in the pores decreases SO_2 removal activity, the SO_2 -captured catalyst/sorbent has to be regenerated at a certain conversion level by water washing or reductive decomposition to recover its activity.

SO_2 removal over V_2O_5/AC consists of two steps: removal and regeneration. The mechanism proposed for SO_2 removal was [9]:

- (1) adsorption of SO_2 on V_2O_5 sites or on AC sites adjacent to V_2O_5 sites;
- (2) activation of SO_2 by V_2O_5 to form a $VOSO_4$ -like intermediate;
- (3) reaction of the $VOSO_4$ -like intermediate with O_2 to form SO_3 and V_2O_5 ;

* Corresponding author at: State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, P.O. Box 165, Taiyuan, Shanxi 030001, PR China. Tel.: +86 351 4053091; fax: +86 351 4053091.

E-mail address: zyl@public.ty.sx.cn (Z. Liu).

- (4) migration of SO_3 over the surface, reaction of SO_3 with H_2O to form H_2SO_4 , and storage of H_2SO_4 in the pores of AC.

Apparently, SO_2 removal mechanism of $\text{V}_2\text{O}_5/\text{AC}$ is different from that of AC/ACF in catalytic oxidation of SO_2 . In the absence of V_2O_5 , oxygen functional groups on AC/ACF are responsible for SO_2 oxidation, which is effective at temperatures below 100°C . However, in the presence of V_2O_5 , V_2O_5 is responsible for SO_2 oxidation, especially at temperatures around 200°C . In addition to the role of V_2O_5 , the higher SO_2 removal activities of $\text{V}_2\text{O}_5/\text{AC}$ should also be related to the properties of AC since poor SO_2 removal activity was found for V_2O_5 supported on other materials. In this regard, it is interesting to quantify the effects of V_2O_5 and AC on SO_2 removal at around 200°C . This information is of importance for validating catalytic mechanism of $\text{V}_2\text{O}_5/\text{AC}$.

2. Experimental

2.1. Preparation of catalysts

A coal-derived coke (a commercial product of Xinhua Chemical Company, Taiyuan, China) is used as the raw material. The coke is activated in steam at 850°C for 40, 60, 80, 120 and 160 min to yield a variety of ACs with different surface textures. These ACs are named AC40, AC60, AC80, AC120 and AC160 according to the activation time. To eliminate possible influence of minerals (ash), all the AC samples are subjected to acid wash at 60°C for 12 h using an aqueous solution containing 2 mol/l HCl and 2 mol/l HF. The demineralized AC samples (with ash contents $<0.6\%$) are marked with a prefix DM-. To introduce oxygen functional groups to AC's surface, DM-AC80 is treated with an aqueous HNO_3 solution (2 mol/l) at 60°C for 12 h and then washed with distilled water to neutral and dried at 110°C for 5 h. The resulting sample is named NDM-AC80.

The $\text{V}_2\text{O}_5/\text{AC}$ catalysts are prepared by pore volume impregnation of the AC supports with an aqueous solution containing ammonium metavanadate and oxalic acid. The catalysts are then dried at 50°C for 5 h and at 110°C overnight and subsequently calcined in N_2 at 500°C for 5 h and then exposed in air at 250°C for 5 h. The catalysts are named according to their components. V2/(DM-AC80) refers to DM-AC80 supported with 2 wt.% V_2O_5 , for example.

2.2. Activity measurement

A fixed bed reactor is used for SO_2 removal experiment. The feed contains 1600 ppm SO_2 , 500 ppm NO, 4.5% O_2 , 2.5% H_2O , balance N_2 and 500 ppm NH_3 . It should be pointed out that 500 ppm NO is introduced into the feed to simulate flue gas and 500 ppm NH_3 is to reduce NO. Our previous work [9] found that NO and NH_3 in the feed do not influence SO_2 removal over $\text{V}_2\text{O}_5/\text{AC}$. Therefore, SO_2 removal behavior is investigated in the presence of NO and NH_3 .

To identify the different roles of O_2 and the lattice oxygen of V_2O_5 in SO_2 removal, O_2 -response experiments were

Table 1
BET surface area and pore volume of the catalysts

Catalyst	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Pore volume ($<1\text{ nm}$) (cm^3/g)
V2/(DM-AC40)	306	0.13	0.09
V2/(DM-AC60)	405	0.19	0.12
V2/(DM-AC80)	621	0.26	0.16
V2/(DM-AC120)	700	0.27	0.15
V2/(DM-AC160)	496	0.26	0.12
V2/AC80	609	0.28	0.17
V2/(NDM-AC80)	631	0.28	0.16

performed in the fix bed reactor. The feed contains 500 ppm SO_2 , 4.5% O_2 (when used), 2.5% H_2O and balance N_2 . All the experiments are made at 200°C with 3 g catalysts and a total flow of 400 ml/min, corresponding to a space velocity of 8000 l/kg h. SO_2 , NO and O_2 concentrations of the feed and the effluent are measured on line by a flue gas analyzer (Dräger, Germany).

2.3. Characterizations of physical and chemical properties

BET surface area and pore volume of the $\text{V}_2\text{O}_5/\text{AC}$ samples are determined by N_2 adsorption at 77 K using a surface analyzer (ASAP2000, Micromeritics). Pore size distribution is calculated based on Density Functional Theory (DFT). BET surface area and pore volume of the catalysts are shown in Table 1.

X-ray diffraction (XRD) pattern of the $\text{V}_2\text{O}_5/\text{AC}$ samples are obtained on a Rigaku computer-controlled D/max 2500X using $\text{Cu K}\alpha$ as the radiation source. The applied current and voltage are 30 mA and 40 kV, respectively.

C, H, O, N and S contents in ACs are measured on an element analyzer (Vario EL, Germany). It should be pointed out that O content in ACs is the amount of surface oxygen and the amount of lattice oxygen can be estimated according to V_2O_5 loading (5 lattice oxygen in 1 V_2O_5 molecule). Results show that the former is higher than 2.3 wt.% and the latter is no more than 0.9 wt.%.

Mineral matter characterization was carried out according to GB/T 1574-1995 method designated for analysis of ash composition of coals.

3. Results and discussion

3.1. The role of lattice oxygen in V_2O_5 in SO_2 removal

Fig. 1 shows SO_2 removal behavior of DM-AC80 supported with different amounts of V_2O_5 . SO_2 removal activity of the support DM-AC80 is very low, but the activity increases greatly with an increase in V_2O_5 loading. This indicates the importance of V_2O_5 in SO_2 removal, although the amount of lattice oxygen in V_2O_5 , no more than 0.9 wt.% (V2/(DM-AC80)), is much lower than that of surface oxygen, 2.75 wt.%.

In our previous work [9], it was found that an adsorption peak of VOSO_4 was observable on the used $\text{V}_2\text{O}_5/\text{AC}$ through Fourier transformed infrared spectroscopy (FTIR) and dis-

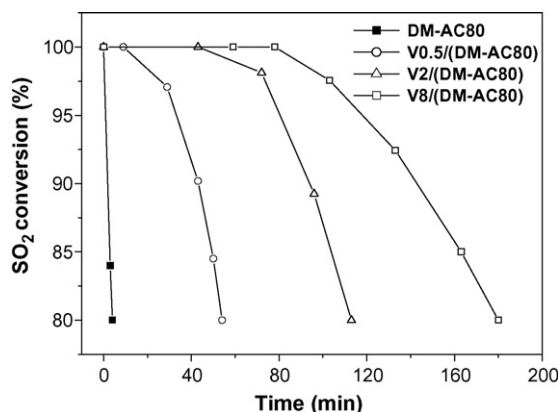


Fig. 1. SO_2 conversions of DM-AC80-supported V_2O_5 catalysts. Reaction conditions: 1600 ppm SO_2 ; 500 ppm NO ; 500 ppm NH_3 ; 4.5% O_2 ; 2.5% H_2O ; 200 °C.

appeared after exposition to an $\text{O}_2 + \text{H}_2\text{O}$ environment at 200 °C. These suggest that V_2O_5 chemically absorbs SO_2 to form a VOSO_4 -like intermediate firstly, and then the intermediate reacts with O_2 to form SO_3 [9]. To differentiate the effect of these two steps on SO_2 removal activity, O_2 -response experiments are carried out in this work, where O_2 is removed from the feed at a time on stream of 5 min and then resumed at a SO_2 conversion of 60%. The removal of O_2 aims to terminate reactions between the VOSO_4 -like intermediate and O_2 , and to evaluate the amount of intermediate formed. The results in Fig. 2 show that SO_2 conversion of DM-AC80 drops quickly before the O_2 interruption while SO_2 conversions of all the V_2O_5 -loaded DM-AC80 catalysts maintain at 100% for some time after the O_2 interruption (this time is defined as breakthrough time). Additionally, a higher V_2O_5 loading results in a longer breakthrough time and a slower decrease in SO_2 conversion after the SO_2 breakthrough. When O_2 is resumed to the feed, SO_2 conversions of all V_2O_5 -loaded samples rise to 100% at the same rate, regardless of the differences in V_2O_5 loading or the amounts of VOSO_4 -like intermediate formed. These data indicate that the reaction between the VOSO_4 -like intermediate and gaseous O_2 is very fast and does not limit the overall SO_2 removal process under the conditions used. In other words, the formation rate of VOSO_4 -like intermediate is the limiting step, which is influenced by V_2O_5 loading.

It is reasonable to believe that lattice oxygen in V_2O_5 is responsible for the formation of VOSO_4 -like intermediate. The amount of lattice oxygen involved in the intermediate formation at each V_2O_5 loading can be estimated from the amount of SO_2 adsorbed during the O_2 -interruption, which is determined by extrapolation of the decreasing SO_2 conversion after the breakthrough to the horizontal axis (the dash lines in Fig. 2) and integration of the area under the SO_2 conversion curve. Since the amount of residual O_2 in the system after the O_2 -interruption is small (at a space velocity of 8000 l/kg h) and the support DM-AC80 absorbs little SO_2 after the O_2 -interruption, the amount of SO_2 determined from the integration (in mole, termed δSO_2) corresponds to the amount of lattice oxygen used for the formation of VOSO_4 -like

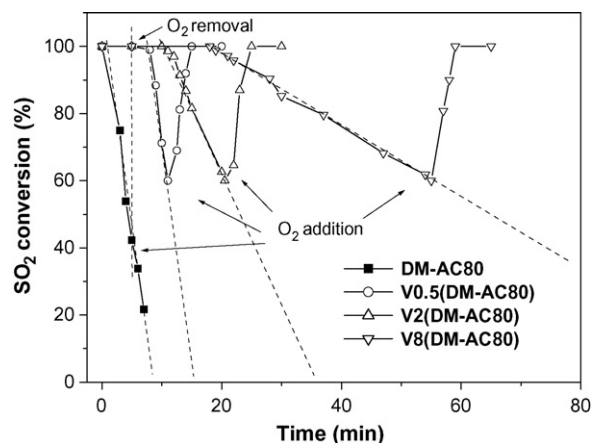


Fig. 2. O_2 -response experiments during SO_2 removal over DM-AC80-supported V_2O_5 catalysts. Reaction conditions: 500 ppm SO_2 ; 2.5% H_2O ; 4.5% O_2 (when used); 200 °C.

intermediate. This type of lattice oxygen is termed “effective lattice oxygen” (ELO in short) to distinguish them from all the oxygen in V_2O_5 . If one SO_2 molecule combines one ELO atom in the intermediate formation, the amount of ELO equals δSO_2 (in mole). Fig. 3 shows the amount of ELO determined for the three V_2O_5 -loaded catalysts (solid squares). If one V_2O_5 molecule provides one ELO atom, a straight line can also be obtained (the dash line in Fig. 3). Apparently, the amount of ELO increases with an increase in V_2O_5 loading. In addition, the amount of ELO at a low V_2O_5 loading of 2.8×10^{-5} mol/g (0.5 wt.%) is very close to the dash line while those at higher V_2O_5 loadings are far from the dash line. These may indicate that the highest usage of O atom in a V_2O_5 molecule is about one, but the O usability decreases with increasing V_2O_5 loading. This is understandable because a lower V_2O_5 loading may result in finer dispersion of V_2O_5 on AC while a higher V_2O_5 loading usually results in more agglomerated V_2O_5 particles and relatively less surface V_2O_5 . To show the difference in particle size of V_2O_5 , XRD analyses were performed. However, there are no diffraction peaks of V_2O_5 for all the samples and no valuable information can be obtained.

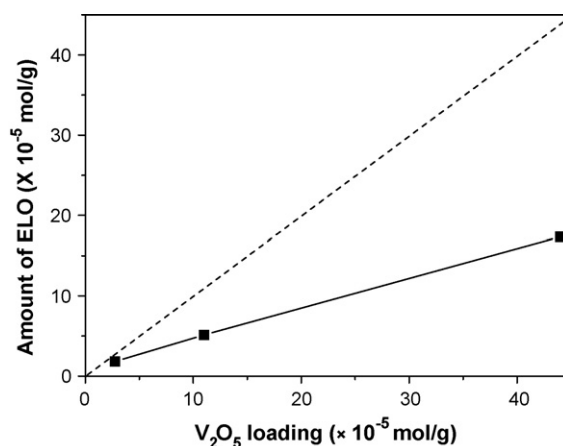


Fig. 3. Amount of effective lattice oxygen (ELO) vs. V_2O_5 loading over DM-AC80.

The information obtained so far indicates that one surface V_2O_5 molecule provides one ELO atom, which adsorbs and oxidizes one SO_2 molecule to form one $VOSO_4$ -like intermediate. In this process, the valence of V changes from V^{5+} to V^{4+} , which is consistent with the XPS analysis reported by Ma et al. for the same type of catalyst [10].

3.2. Usability of ACs' pores and its relation with V_2O_5

Since the role of V_2O_5 on SO_2 removal is to provide lattice O to oxidize SO_2 to a $VOSO_4$ -like intermediate, the differences in V_2O_5 loading affect only the rate of SO_2 oxidation. However, the data in Fig. 1 show that the rate of SO_2 oxidation is high enough for all the V_2O_5 -loaded catalysts because their initial SO_2 conversions are all 100%. This suggests that the different SO_2 removal behavior of the V_2O_5 -loaded catalysts results from other factors. According to the proposed SO_2 removal mechanism reported by Ma et al. [10], the SO_3/H_2SO_4 storage capacity of AC is a possible factor.

It is logical to believe that not all the pores in the AC is usable for storage of SO_3/H_2SO_4 , and only the pores in the vicinity of V_2O_5 sites are able to accept and store SO_3/H_2SO_4 migrated from V_2O_5 sites. A lower V_2O_5 loading yields fewer and smaller V_2O_5 sites and thus fewer pores for storage of SO_3/H_2SO_4 and therefore a lower SO_2 removal activity. A higher V_2O_5 loading yields more and possibly larger V_2O_5 sites, and thus more pores to be accessible for storage of SO_3/H_2SO_4 . It is worth to note that at higher V_2O_5 loadings, some of the pores in the vicinity of one V_2O_5 site may be close to other V_2O_5 sites. This hypothesis is shown in Fig. 4.

To estimate the pore usability of AC in SO_2 removal process, the volumes of H_2SO_4 stored, termed “effective pore volume” or EPV in short, are calculated by subtracting the amounts of SO_2 combined with ELO from corresponding SO_2 capacities. The SO_2 capacities, termed ΔSO_2 , are determined from Fig. 1 as the areas between SO_2 conversion curves of V_2O_5 -loaded catalysts and that of the support (DM-AC80). Fig. 5 shows that EPV increases with an increase in V_2O_5 loading but the values are small, even much smaller than the volume of pores with diameters less than 1 nm. This phenomenon agrees with the hypothesis in Fig. 4.

The discussions presented so far show that the role of V_2O_5 in V_2O_5/AC in SO_2 removal is to provide lattice O for SO_2 oxidation, and to serve as a center for distribution of SO_3/H_2SO_4 to the AC's pores in its vicinity. To show these roles more clearly, the catalyst-mass-based parameters ELO, EPV and ΔSO_2 presented above are divided by the loading of V_2O_5 (in mole)

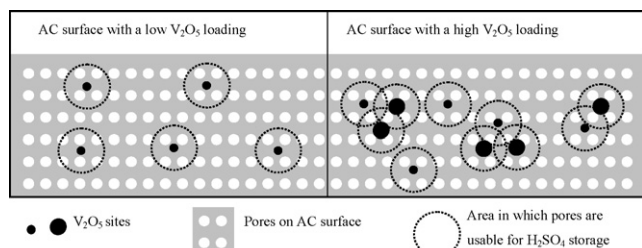


Fig. 4. Hypothetic mapping of V_2O_5/AC catalyst surface.

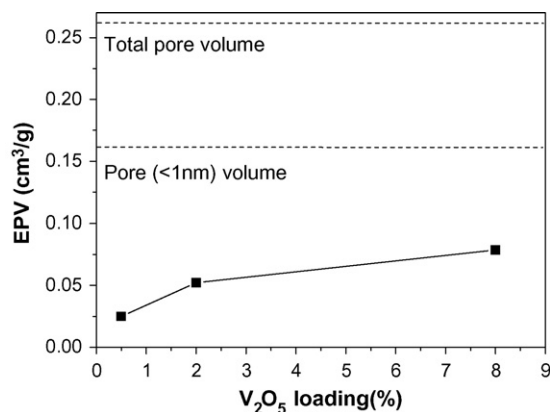


Fig. 5. Effective pore volume (EPV) of the catalysts vs. V_2O_5 loading.

in the catalysts, and the results are shown in Fig. 6. The values of ELO/V_2O_5 , EPV/V_2O_5 and $\Delta SO_2/V_2O_5$ all decrease with an increase in V_2O_5 loading, but the decreases in EPV/V_2O_5 and $\Delta SO_2/V_2O_5$ are relatively faster than that in ELO/V_2O_5 . This indicates that V_2O_5 sites preferentially locate at certain parts of AC surface, resulting in less increase in EPV in comparison to an increase in ELO when V_2O_5 loading is increased. This is also demonstrated by the ratios of EPV/ELO , which are 1330, 990 and 530 cm^3/mol for $V0.5/(DM-AC80)$, $V2/(DM-AC80)$ and $V8/(DM-AC80)$, respectively. All these information indicate that the decrease in SO_2 conversion in the later stage of SO_2 removal as shown in Fig. 1 is influenced mainly by the EPV, which is affected by the distribution of V_2O_5 on the AC surface.

3.3. Effects of ACs' physical and chemical properties on EPV

It is important to note that EPV is still a superficial parameter of AC. It may depend not only on volume of pores available for H_2SO_4 storage but also on surface properties which possibly influences migration of SO_3/H_2SO_4 from V_2O_5 sites to nearby pores.

3.3.1. Effects of ACs' physical properties on EPV

Fig. 7 shows SO_2 removal behavior of various V_2O_5/AC catalysts with 2 wt.% V_2O_5 but different AC supports. As

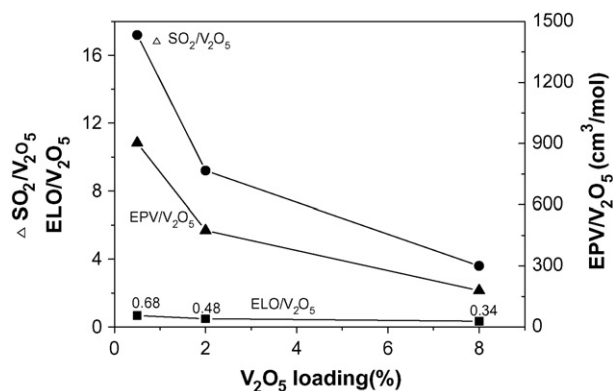


Fig. 6. Mole ratio of ELO/V_2O_5 , $\Delta SO_2/V_2O_5$ and EPV/V_2O_5 vs. V_2O_5 loading on DM-AC80.

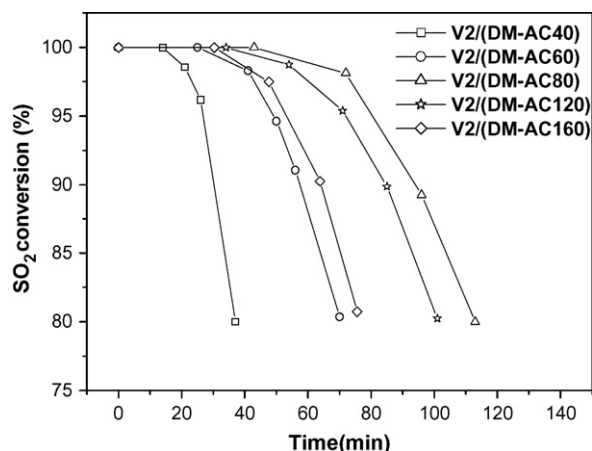


Fig. 7. SO_2 conversions of the catalysts with 2 wt.% V_2O_5 but different ACs. Reaction conditions: 1600 ppm SO_2 ; 500 ppm NO ; 500 ppm NH_3 ; 4.5% O_2 ; 2.5% H_2O ; 200 °C.

stated in the experimental section, these AC supports were made from the same coke but subjected to steam activation at 850 °C for different periods of time, which ensures that the differences of ACs are mainly in pore texture. The results in Fig. 7 apparently indicate that the SO_2 removal capacity increases with an increase in steam activation time from 40 to 80 min, but then decreases with a further increase in steam activation time to 160 min. To see whether the amount of ELO changes with the steam activation time, O_2 -response experiments are performed on V2/(DM-AC60), V2/(DM-AC80) and V2/(DM-AC120) and the results are shown in Fig. 8. As expected, the three catalysts show the same behavior, indicating the same amount of ELO. This indicates that the steam activation time of AC has little effect on distribution of V_2O_5 and the different SO_2 behaviors in Fig. 7 can be attributed mainly to the difference in EPV.

Fig. 9a shows the relations of EPV determined from Fig. 7 and physical properties of the catalysts with activation time. Among the four curves, the changes in EPV seem correlating well only with the changes in volume of pores smaller than 1 nm. This is understandable because H_2SO_4 is mainly stored in

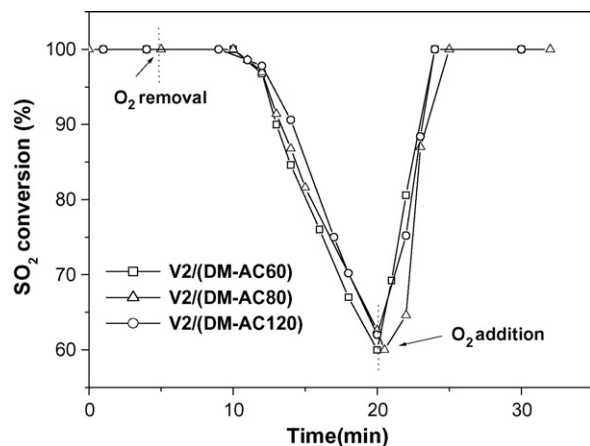


Fig. 8. O_2 -response experiments during SO_2 removal over V2/(DM-AC60), V2/(DM-AC80) and V2/(DM-AC120). Reaction conditions: 500 ppm SO_2 ; 2.5% H_2O ; 4.5% O_2 (when used); 200 °C.

the micro-pores as reported in the literature [4,18]. Fig. 9b correlates EPV with volume of pores smaller than 1 nm for all the catalysts with 2 wt.% V_2O_5 . It is clear that the data of the catalysts with DM-AC as supports form a straight line, indicating a strong relation between EPV and pores smaller than 1 nm.

The significant deviations for V2/AC80 (not subjected to the de-mineralization treatment) and V2/(NDM-AC80) (subjected to a HNO_3 treatment after the de-mineralization treatment) from the straight line indicate that chemical properties also affect the value of EPV.

3.3.2. ACs' chemical properties and its relation with EPV

Fig. 10a shows SO_2 conversion behaviors of V2/AC80, V2/(DM-AC80) and V2/(NDM-AC80) as well as that of the supports. The supports themselves (filled symbols) show little SO_2 removal capacity, but they do make significant differences in SO_2 removal behavior when 2 wt.% V_2O_5 is loaded onto them (open symbols). Compared to V2/AC80, the de-mineralized support increases the SO_2 removal capacity (see V2/(DM-AC80)) but a further HNO_3 treatment decreases the SO_2 removal capacity (see V2/(NDM-AC80)). To see whether the differences in AC supports affect ELO, O_2 -response experiments are performed on these V_2O_5 -loaded catalysts. The results in Fig. 10b shows similar amounts of ELO for the three catalysts, which indicates again that the differences in SO_2 removal behaviors of the catalysts result

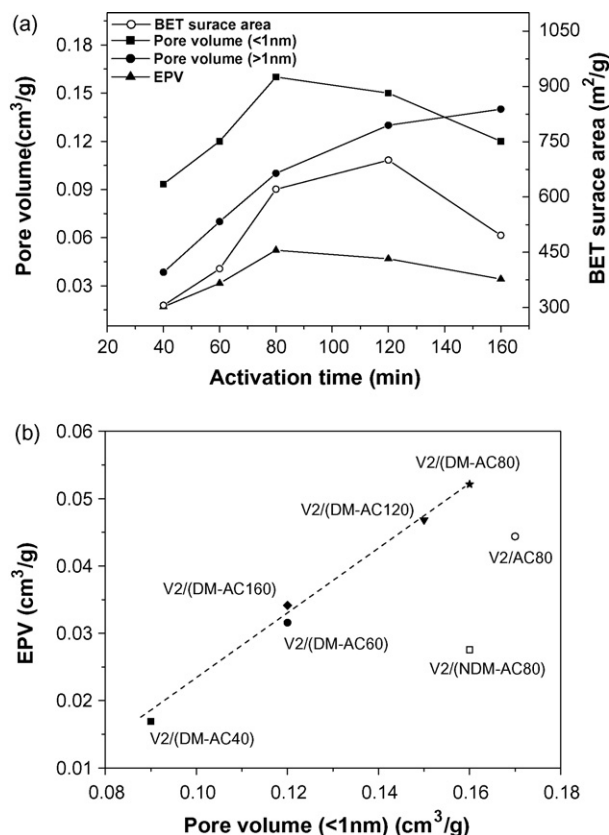


Fig. 9. (a) BET surface area, pore volume and EPV vs. activation time; (b) EPV vs. pore volume (<1 nm).

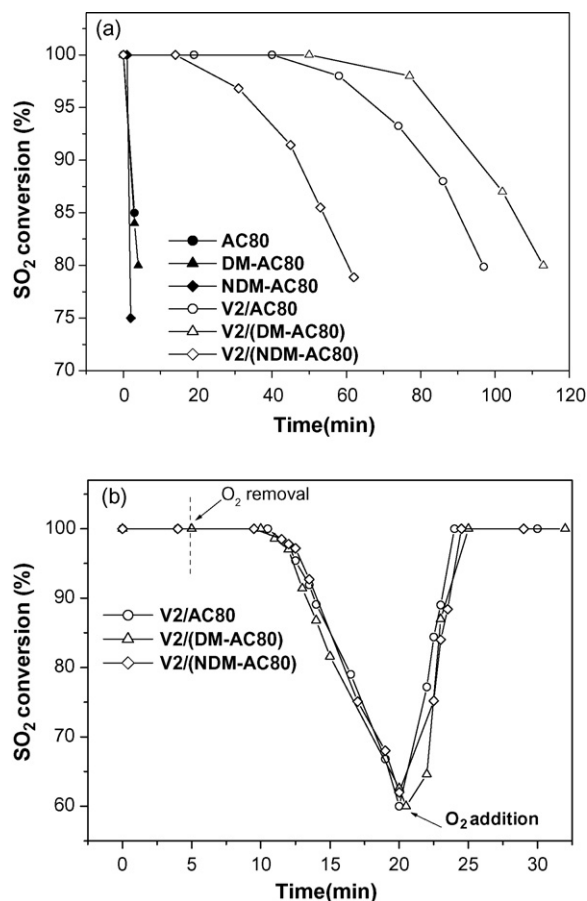


Fig. 10. Effect of AC treatments on SO₂ removal. (a) SO₂ conversions at 200 °C; reaction conditions: 1600 ppm SO₂; 500 ppm NO; 500 ppm NH₃; 4.5% O₂; 2.5% H₂O and (b) O₂-response experiment; reaction conditions: 500 ppm SO₂; 2.5% H₂O, 4.5% O₂ (when used); 200 °C.

from the differences in EPV of the AC supports. Since these AC supports show similar physical properties (see Table 1), their differences should mainly be attributed to differences in chemical properties. Table 2 shows that the demineralization of AC80 results in a significant reduction in ash content, from 8.2% to 0.25%, but not in the contents of other elements (see AC80 and DM-AC80). Treatment of DM-AC80 with HNO₃ results in significant increases in O and N contents, from 2.75% to 5.85% and from 0.79% to 1.50%, respectively, but little changes in contents of other compo-

Table 2
Elemental and ash analyses of the different activated cokes (wt.%)^a

Sample	C	H	O ^b	N	S	Ash
DM-AC40	94.87	0.71	2.64	0.64	0.56	0.58
DM-AC60	95.58	0.61	2.31	0.60	0.57	0.33
DM-AC80	94.99	0.68	2.75	0.79	0.54	0.25
DM-AC120	94.34	0.79	3.01	0.86	0.54	0.46
DM-AC160	95.26	0.52	2.54	0.68	0.61	0.39
AC80	87.36	0.59	2.56	0.74	0.55	8.20
NDM-AC80	91.20	0.69	5.85	1.50	0.54	0.22

^a Moisture-free basis.

^b By difference.

nents. These data suggest that the minerals, O-containing and N-containing functional groups in AC prevent migration of SO₃/H₂SO₄. This finding indicates that oxygen functional groups play different roles in SO₂ removal at different temperatures.

4. Conclusions

Compared to activated cokes (AC), V₂O₅/AC are more active for SO₂ removal from flue gases at temperatures around 200 °C. The role of V₂O₅ is to provide lattice oxygen to absorb and oxidize SO₂ into a VOSO₄-like intermediate. The intermediate then reacts with gaseous O₂ to form SO₃ and V₂O₅. The amount of lattice oxygen in V₂O₅ used for the intermediate formation (this type of lattice oxygen is termed ELO) is dependent on the V₂O₅ loading and independent of the properties of AC support under the conditions used. The maximum amount of ELO is one atom per V₂O₅ molecule at low V₂O₅ loadings.

The role of AC is to store the SO₃/H₂SO₄ from V₂O₅ sites. Only the pores in the vicinity of V₂O₅ sites are available for storage of SO₃/H₂SO₄. The volume of these pores, termed EPV, is influenced by the physical properties of AC support, which is proportional to but significantly smaller than the volume of pores smaller than 1 nm. The EPV is also influenced by the chemical properties of AC support. Minerals, O-containing and N-containing functional groups in AC may inhibit migration of SO₃/H₂SO₄.

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